Effect of Bleached Eucalyptus and Pine Cellulose Nanofibers on the Physico-Mechanical Properties of Cartonboard

Ana Balea, Ángeles Blanco,* M. Concepción Monte, Noemi Merayo, and Carlos Negro

Extending the limits of paper recycling by increasing the number of recycling cycles results in decreased mechanical properties due to the irreversible hornification of cellulose fibers. This process alters the fiber structure and properties because of the repeated chemical and mechanical treatments that occur during wetting and drying. As a result, poor tensile strength is the main source of customer complaints to paper manufacturers. Cellulose nanofibers (CNF) from bleached eucalyptus and pine pulps were investigated as potential strength additives because of their proven contribution to interfiber bonding. These results were compared to the results obtained using different families of strength additives. The effects on the mechanical properties of recycled old corrugated containers were studied by measuring bursting, tensile, and short span compressive strength. Cellulose nanofibers and cationic polyacrylamide (cPAM) improved the mechanical strength properties when they were added at doses around 4 wt.%. A combination of CNF and cPAM was also tested. The effects of the combined additives were not as high as expected compared to the results achieved individually. The CNF from pine pulp resulted in the highest increase in bursting index when combined with cPAM, achieving an increase of over 93%. The combination of CNF from eucalyptus pulp and cPAM increased the bursting index over 60%.

Keywords: Paper strength additives; Cellulose nanofiber; Old corrugated containers; Recycled paper; Mechanical properties

*Contact information: Department of Chemical Engineering, Complutense University of Madrid, 28040 Madrid, Spain; *Corresponding author: ablanco@ucm.es*

INTRODUCTION

Over the past several decades, the recovery of paper and the utilization of recovered paper have increased throughout the world. As a result of concerns about environmental issues, saving energy, population growth, and the shortage of wood supplies, the importance of recycling and the utilization of secondary fibers has been recognized (Miranda *et al.* 2010; Blanco *et al.* 2013). In Europe, the paper recycling rate has reached 71.7%, and the total amount of paper collected and recycled has remained stable at just over 58 million tons, despite the decreasing consumption of paper (CEPI 2014). Currently, based on the utilization and recovery rates, old corrugated containers (OCC) are the most significant category of recycled papers.

By increasing the number of recycling cycles, the quality of the fibers gradually decreases, mainly because of the hornification of the cellulose fibers causing irreversible changes in the fiber structure and properties. The hornification is caused by the repeated chemical and mechanical treatments that occur during wetting and drying. Therefore, the major problem with the recycling of OCC is the loss of strength (Nazhad and Sodtivarakul 2004; Li *et al.* 2010).

Beating or refining is the most common method used to improve the strength of paper. By applying shear forces to the fibers, more fibrillated fibers are created, improving mechanical entanglement, hydrogen bonds, and fiber-to-fiber joint strength. This allows the formation of a fibrous network with some improved mechanical properties, but it is clearly detrimental to others, slowing the drainage rate, increasing energy consumption, and decreasing the tear resistance and opacity of the finished paper (Nazhad 2005; Hubbe *et al.* 2007; Miranda *et al.* 2013).

Cationic starch (CS) (Ghasemian *et al.* 2012) and synthetic polymers based on polyacrylamides (PAM) (Laleg and Pikulik 1991; Lu *et al.* 2002; Wang and Jing 2014) are the most commonly used strength additives in papermaking. Cationic starch and PAM also provide other benefits, such as better retention of fines and fillers, fast drainage, and reduction of wastewater pollution. Nevertheless, CS is normally supplied in a solid form, which requires an investment in equipment, along with the added cost of dedicated personnel to run the equipment. Another drawback is the tendency of CS to promote biological growth and deposits. Moreover, because of competition with the food industry, starch prices have significantly increased, and synthetic alternatives have become more attractive. Cationic PAM (cPAM) products are self-retaining on cellulose fibers, but they can be sensitive to colloidal and dissolved substances such as anionic trash, especially in recycled fibers. A high cationic charge can overcome these problems, but cPAMs tend to be expensive because of the high cost of cationic monomers (Yamauchi and Hatanaka 2002; Lindström *et al.* 2005)

Other polyelectrolytes have also been investigated for their potential to improve the dry and wet strength of paper, such as glyoxalated polyacrylamides (GPAM) (Yuan *et al.* 2011; Yuan and Hu 2012), polyvinylamine (PAV) (DiFlavio *et al.* 2005; Chen *et al.* 2008; Marais and Wagberg 2012; Wang *et al.* 2015), and melanine-formaldehyde resins (MF) (Pelton 2004; Lindström *et al.* 2005). The results showed that the tensile and bursting strength properties were improved less than 50%, and the highest improvements were reached with doses that would not be profitable for papermaking use.

Consequently, many researchers are focused on the feasibility of using natural and/or synthetic polymers to improve the strength of recycled paper and board. However, poor tensile strength is the main source of customer complaints to paper manufacturers, and alternative methods for improving the strength of recycled fibers are still needed. Moreover, a comparison study of the main strength additives for recycled board fibers using the same recycled raw material and protocols is still needed. Additionally, other physical properties such us porosity must be taken into account to fulfill the required board specifications, according to its use.

In this context, new strategies to improve interfiber bonding must be explored, such as the use of cellulose nanofibers (CNF) (Osong *et al.* 2016). Cellulose nanofibers are receiving great attention because of their variety of applications, renewable nature, potential high availability, and complete biodegradability (Johansson *et al.* 2012). Among these applications, the use of CNF for papermaking presents interesting properties, such as a large specific surface area and high aspect ratio. Cellulose nanofibers also improve bond degree and paper strength, along with reducing the porosity of the final paper sheet (Eriksen *et al.* 2008; Taipale *et al.* 2010; Delgado-Aguilar *et al.* 2014). Therefore, CNF are a potential candidate to reinforce OCC strength because of their proven contribution to improving interfiber bonding. Although there are several studies supporting the ability of added CNF in composites or in paper to provide reinforcement, no studies have been published on the effect of the use of CNF as an alternative to enhance the strength properties of recycled OCC.

The main objective of this research was to compare the efficiency of different products in improving the strength of recycled OCC. First, different families of strength additives (PAM, PAV, MF, and CS) were evaluated to determine the optimal dose for improving both mechanical strength and flocculation behavior. The results of these strength additives were then set as references to evaluate CNF as a novel potential strength additive. Cellulose nanofibers from bleached eucalyptus (CNF-E) and pine (CNF-P) pulps were then added to the recycled OCC furnish, and the handsheet properties were investigated in terms of mechanical enhancement. In addition, combinations of the best strength additive and CNF were examined to determine the optimal combination for improving mechanical strength. The effect on porosity was also evaluated.

EXPERIMENTAL

Cellulose Nanofibers

Cellulose nanofibers were obtained from two different sources of cellulose: (i) never-dried, refined *Eucalyptus globulus* ECF bleached kraft pulp (CNF-E); and (ii) never-dried, bleached pine pulp (CNF-P), manufactured by Torraspapel, S.A. (Zaragoza, Spain).

The CNF were obtained by TEMPO-mediated oxidation with 5 mmol of NaClO per g of dry pulp. The oxidation conditions were identical to those of Saito *et al.* (2007). Once the pulp was oxidized, a filtration cleaning process was done using distilled water to reach a pH value around 7. Finally, six steps of homogenization at 600 bar were applied in a laboratory homogenizer PANDA PLUS 2000 manufactured by GEA Niro Soavy (Parma, Italy). The CNF were characterized according to the methodology described by Balea *et al.* (2016). Table 1 lists the properties of both types of CNF produced in this study.

Table 1. Characterization of Eucalyptus and Pine Cellulose Nanofibers

Parameter	Unit	CNF-E	CNF-P
Yield	%	>95	>95
Carboxylic Groups	mmol/g	0.59	0.75
Cationic Demand	meq/g	1.139	0.902
Transmittance	400 nm (%)	83.5	77.5
	800 nm (%)	94.8	88.9
Polymerization Degree	Monomeric Units	440	300

Strength Additives

The suppliers and the characteristics of the strength additives, categorized into different families, are shown in Table 2.

The PAM, PAV, and cMF were diluted in distilled water to a concentration of 10 wt.% expressed on the commercial product before use. The CS solution was prepared at 6 g/L; 3 g of dry CS were heated to 90 to 95 °C in 200 mL of water under stirring with a magnet and propeller in a beaker. Afterwards, the beaker was covered with aluminum foil, and the solution was kept at 90 °C for 15 to 30 min. Finally, the CS solution was chilled to ambient temperature and diluted to 500 mL.

Table 2. Characteristics of the Strength Additives (Based on the Manufacturers' Specifications)

Family	Strength Additives		Supplier	Form of Delivery	Charge	Solid Content (%)
PAMs	Cationic Polyacrylamide	cPAM	NTL	Liquid	Cationic	16
	Cationic Glyoxalated Polyacrylamide	GPAM-1	Kemira	Liquid	Cationic	8-20
		GPAM-2	Kemira	Liquid	Cationic	8-20
PAVs	Cationic Polyvinylamine	cPAV-1	BASF	Liquid	Medium Cationic	15-17
		cPAV-2		Liquid	High Cationic	17-19
		cPAV-3		Liquid	Very High Cationic	20-22
	Amphoteric Polyvinylamine	APAV-4		Liquid	Amphoteric	10-12
MF	Cationic Melamine Formaldehyde	cMF	NTL	Liquid	Cationic	43.5
Starch	Cationic Cook-Up Potato Starches	CS	SolAm	Dry	Cationic	100

Pulp and Sheets Preparation

Pulps were prepared through disintegration of 60 g of dry OCC in 2000 mL of tap water (3.0 wt.%) by using a Messmer pulp disintegrator (Mavis Engineering Ltd., London, England) at 30,000 revolutions, according to the ISO 5263-1 standard (2013). The OCC was left to soak at least 24 h before disintegration to favor fiber swelling. Once the pulp was disintegrated, it was diluted to 1.0 wt.% consistency and mixed with the strength additives. When CNF were studied as a strength additive, 30 g of dry OCC were soaked for 24 h and disintegrated with the selected amount of CNF in 2000 mL of water (1.5 wt.% consistency) at 180,000 revolutions in order to maximize the dispersion of the CNF into the pulp suspension. The OCC-CNF pulp was diluted to 1.0 wt.% consistency and stirred for at least 10 min before cationic starch (0.5 wt.%) and silica (0.8 wt.%) were added as retention agents of the CNF (González *et al.* 2012).

Finally, the pulp suspension at 1.0 wt.% was used to prepare handsheets with basis weight of 80 g/m^2 according to the standards ISO 5269-2 (2004) and DIN 54 358 (1981) by using a Rapid-Köthen sheet-former from PTI (Vorchdorf, Austria). These handsheets were conditioned at 25 ºC and 50% humidity for 24 h before physical and mechanical characterization.

Flocculation Trials

Flocculation trials were carried out using a focused beam reflectance measurement (FBRM) M500L probe (Mettler Toledo, Columbus, USA) to monitor the flocculation process of the pulp and to determine the optimal strength additives dose. The FBRM measured the chord length distribution of particles in the suspension, whose evolution enables monitoring of the flocculation process (Blanco *et al.* 2002a,b). To observe this process, 200 mL of pulp suspension at 1.0 wt.% consistency were stirred at 300 rpm, and the strength additives were added at a rate of 0.1 mL every 10 s or in a single dose while the evolution of the chord length distribution was monitored.

Handsheet Characterization

Bursting strength was determined using a Messmer digital hydraulic board burst tester following the ISO 2759 standard (2014). A Messmer compression tester was used to measure the short-span compressive test (SCT) according to the TAPPI 826 pm standard (1992). Porosity and tensile strength were measured using an AUTOLINE 300 from Lorentzen & Wettre (Stockholm, Sweden) following the standards ISO 5636-3 (2013) and ISO 1924-3 (2014), respectively. Bursting strength index (kPa.m^2/g), SCT index (N.m/g), and tensile strength index (kN.m/kg) were calculated using the average grammage of the handsheets.

RESULTS AND DISCUSSION

Optimal Flocculation Dose of Strength Additives

Flocculation trials with single additions of the different strength additives were carried out to evaluate the optimum flocculation dose of each additive, corresponding to the maximum mean chord size (MCS) (Fig. 1).

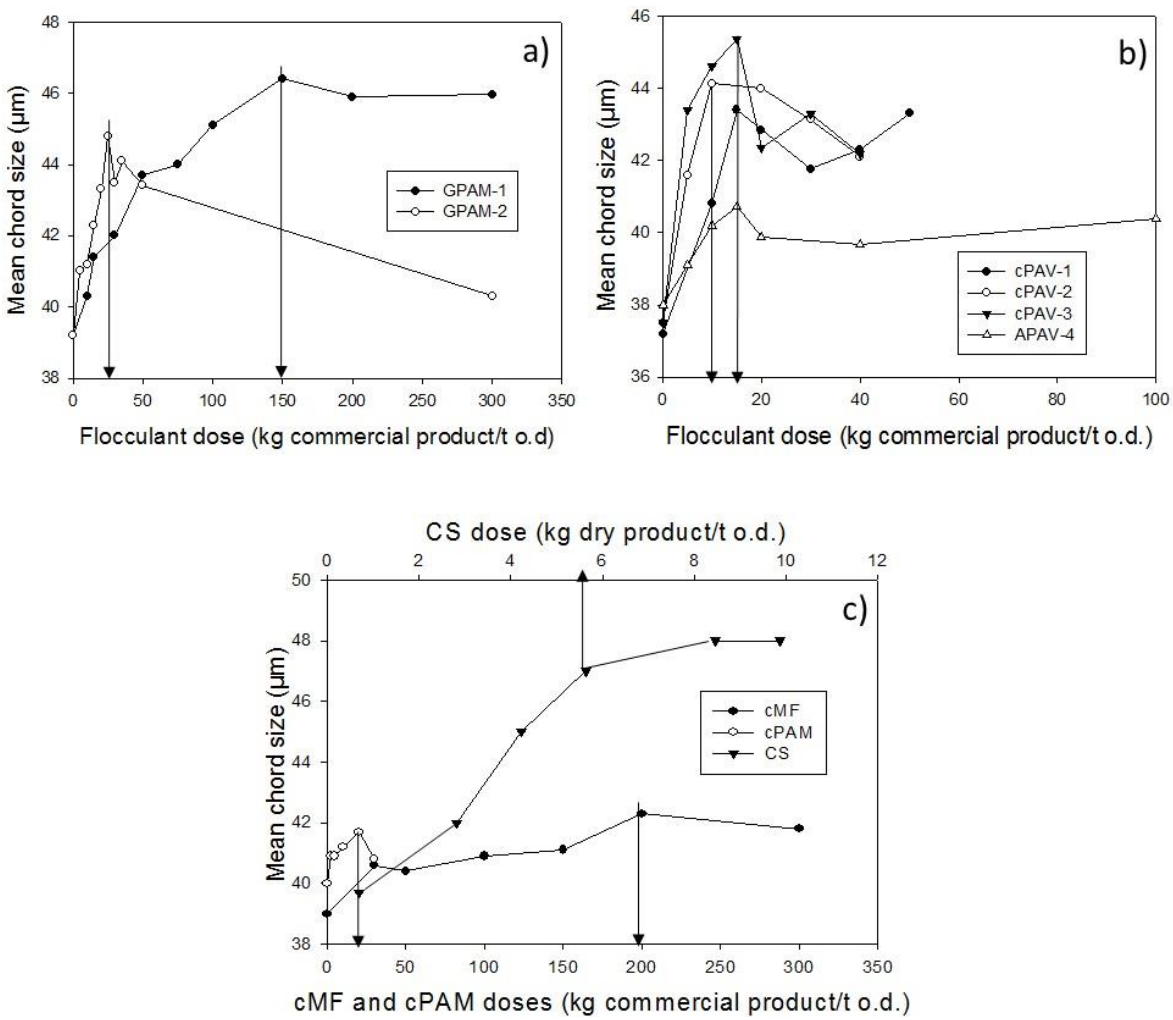

Fig. 1. Evolution of mean chord size with different doses of GPAM (a), PAV (b), cMF, cPAM, and CS (c).

The range of optimal flocculation dose for each strength additive, that is an adequate range of flocculation behavior for papermaking, was selected to perform handsheet preparation and subsequent evaluation of the mechanical properties. However, correlation between flocculation and mechanical properties could not be clearly established because flocculation mechanisms of the additives are different and could have positive or negative impact on paper strength. Therefore, it is important to control wet-end stage and to select optimum additives doses based not only on mechanical properties, but also on flocculation process.

The GPAM resins had the highest optimal flocculation doses at 150 kg/t dry pulp and 25 kg/t dry pulp for GPAM-1 and GPAM-2, respectively. At the optimal flocculation dose, GPAM-1 flocs were larger than GPAM-2 flocs. The flocculation behavior at 300 kg/t dry pulp of polymer was quite different between the GPAM resins, with GPAM-1 flocs being stronger than GPAM-2 flocs, which broke down more easily (Fig. 1a). At the optimal flocculation dose (20 kg/t dry pulp), cPAM had lower maximum MCS than GPAM (Fig. 1c). The flocculation behavior of all cPAV was quite similar. The optimal flocculation dose was 10 to 15 kg of cPAV/t dry pulp, and the maximum MCS increased with the charge of the cPAV from 43.4 μm to 45.4 μm. For APAV, the size of the flocs at the optimal flocculation dose was lower than in cPAV, but APAV kept dry pulp the floc size at doses higher than the optimum (Fig. 1b). When flocculation of the OCC pulp was carried out with cMF, initially, with doses below 200 kg/t dry pulp, the maximum MCS remained stable with a floc size around 40 μm, but the highest MCS was achieved at 200 kg/t dry pulp. The MCS for CS steeply increased with the dose, achieving the maximum MCS at 5.7 kg/t dry pulp. The size of the CS flocs remained stable for doses higher than the optimum (Fig. 1c).

The optimal flocculation dose, lower doses, and higher doses were selected to produce the laboratory handsheets for the evaluation of mechanical properties (Table 3).

Table 3. Optimal Flocculation Doses, Maximum Mean Chord Size, and Selected Chemical Doses for Handsheet Preparation of Strength Additives

Strength Additives	Optimal Flocculation Doses (kg Commercial Product/t Dry Pulp)	Maximum Mean Chord Size (MCS) (μm)	Chemical Doses* For Handsheets Preparation (kg Commercial Product/t Dry Pulp)
cPAM	20	41.7	5 / 10 / 20 /40
GPAM-1	150	46.4	10 / 80 / 150 / 300
GPAM-2	25	44.8	10 / 25 / 50
cPAV-1	15	43.4	10 / 15 / 20
cPAV-2	10	44.1	10 / 15 / 20
cPAV-3	15	45.4	10 / 15 / 20
APAV-4	15	40.7	10 / 15 / 20
cMF	200	42.3	10 / 20 / 50 / 100 / 200 /300
CS	5.6	47.0	1 / 2 / 5 / 10
*Chemical doses units: *e.g.* 20 kg commercial product/ t dry pulp < > 2.0 wt.%			

Effect of the Strength Additives on Mechanical and Physical Properties

Once the optimal flocculation dose was established, the effect of the strength additive dose on the physico-mechanical properties was studied. The optimal flocculation dose, as well as lower and higher doses, was selected to produce the laboratory handsheets for evaluation of the main mechanical properties.

The strength additives had a more significant effect on bursting index than on SCT and tensile indexes, but, in general terms, these three mechanical properties followed the same trend with an increasing dose of the chemical agent studied (Fig. 2).

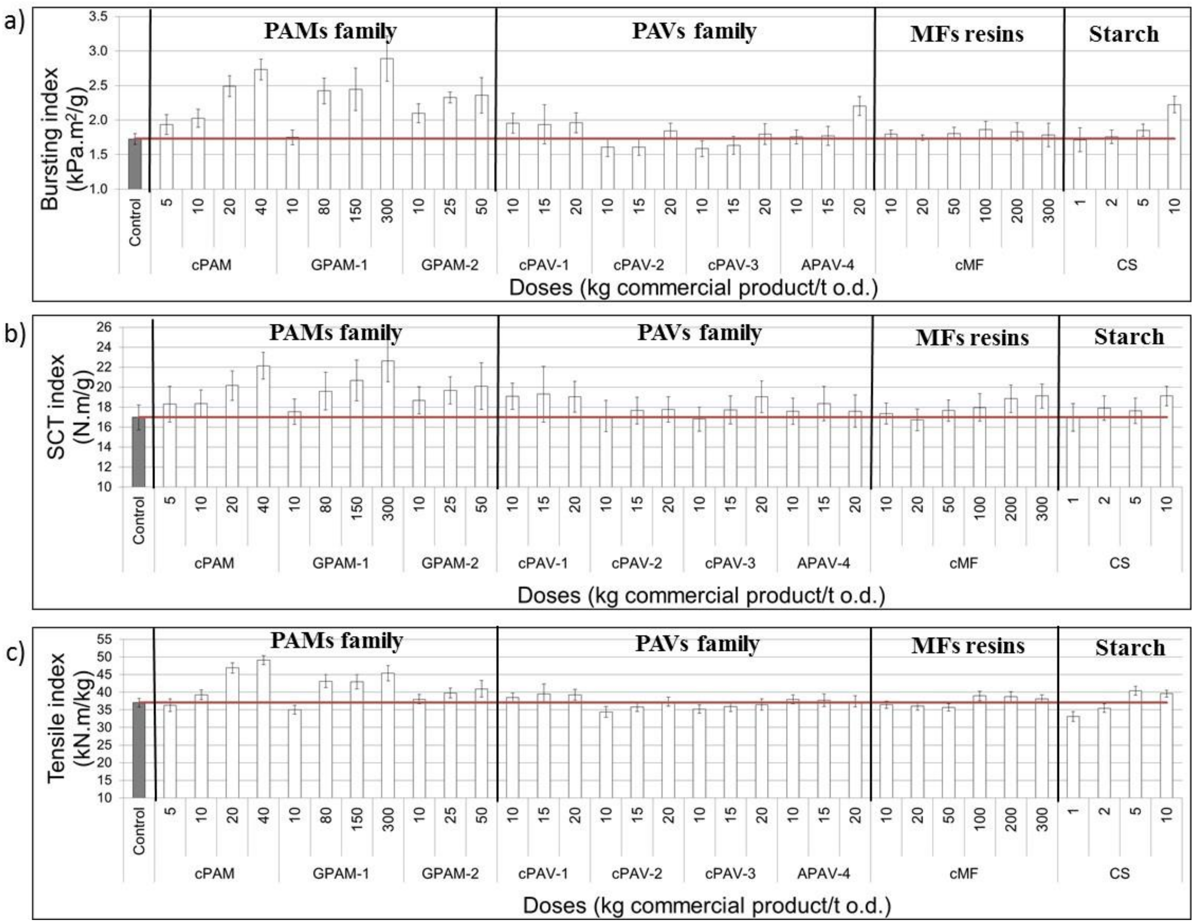

Fig. 2. Bursting (a), SCT (b), and tensile (c) indexes with different doses of additives

The mechanical properties of paper are governed by three main parameters: the fiber strength, the fiber-to-fiber bond strength, and the number of efficient joints per volume (Marais and Wågberg 2012). The cPAM strength additives promoted fiber-to-fiber interactions through covalent and ionic bonds, increasing fiber-to-fiber bond strength. All of the strength properties studied improved with the addition of cPAM. Increasing the cPAM dose from 0 to 20 kg/t dry pulp, resulted in a 44.3% gain in bursting strength index, a 26.5% gain in tensile index, and an 18.7% gain in SCT index. Adding double the cPAM dose, from 20 to 40 kg/t dry pulp, gave only an approximately 10% increase in bursting and SCT strength index properties and a less than 5% increase in tensile index compared to the 20 kg/t dry pulp cPAM addition.

The GPAM strengthening mechanism was primarily through reinforcement of the interfiber joints *via* both hydrogen and covalent bonds (Lindström *et al.* 2005). The GPAM-1, with the highest optimal flocculation dose, provided important increases of the mechanical properties, with an over 40% increase in bursting index and a 16% increase in SCT and tensile index properties at 80 kg/t dry pulp. The highest increases in bursting (67%), SCT (33%), and tensile (22%) indexes were achieved at 300 kg GPAM-1/t dry pulp, but these doses would be extremely high for industrial use. For GPAM-2, the optimal flocculation dose (25 kg/t dry pulp) also achieved the highest improvement in all of the mechanical properties, with an increase of over 30% in bursting index, 16% in SCT index, and 7% in tensile index compared with the reference without any chemical agent. For GPAM-2, the chemical dose that provided the optimal flocculation behavior was also the optimal dose for mechanical enhancement. However, GPAM-1 showed an optimal flocculation dose at 150 kg/t dry pulp, but the optimal dose for mechanical improvement was lower, at only 80 kg/t dry pulp.

For cPAV, the medium cationic charge version (cPAV-1) gave the highest bursting and SCT index with an increase of 12% at the minimum dose tested (10 kg cPAV-1/t dry pulp), with no further improvement in the results at higher doses. The tensile index of cPAV-1 showed the highest increase at 15 kg/t dry pulp (the optimal flocculation dose), decreasing at lower and higher doses. However, high and very high cationic PAV (cPAV-2 and cPAV-3) did not noticeably increase the strength properties, with the optimal strength doses being higher than those for flocculation. The APAV only noticeable enhanced the bursting strength index by 27.6% at 20 kg APAV/t dry pulp. During decades the mechanism by which these amine polymers increase strength has been studied including the analysis of the adsorption isotherms to determine the maximum quantity of PAV that could be adsorbed onto the fiber (DiFlavio *et al.* 2005; Marais and Wågberg 2012). Although higher cationicity of PAV increased dry paper strength (Son and Yong 2005) other parameters such us molecular weight (Marais and Wågberg 2012) or flocculation behaviour should be also considered for mechanical strength properties improvement. MCS (Fig. 1b) increased with the cationic charge of cPAV, and this could affect to the sheet formation and, thus, the mechanical enhancement of the paper.

The cMF did not improve the strength of the OCC pulp when compared to the other additives in similar concentrations. Increasing the dose of the cMF from 0 to 200 kg/t dry pulp, resulted in a nearly 11% gain in SCT index and a less than 4% gain in bursting and tensile indexes. However, these would be extremely high doses for industrial use.

Greater bursting and SCT index results were achieved for CS at 10 kg/t dry pulp, with increases close to 29% and 12.5%, respectively. The maximum tensile index for CS was achieved at the optimum flocculation dose (5 kg/t dry pulp), but all of the strength increases at this dose were much lower than the ones obtained with cPAM at the same concentration.

The physical structure of the handsheets was also studied using the porosity results. The porosity of a liner and/or fluting board affects the rate at which air, vapor, and some liquids will pass through or will be absorbed into the fiber substrate. The porosity using different cPAM, APAV, cMF, and CS doses was similar to the reference pulp without any chemical agent, maintaining the physical structure of the sheet. However, GPAM and cPAV modified the porosity of the sheets compared with the reference pulp. The highest porosity was achieved with GPAM-1 at very high doses (150 and 300 kg/t). On the other hand, for PAVs family the highest porosity was obtained with cPAV, where higher flocs probably induced a higher pore size distribution in the handsheets (Fig. 3). Highly porous boards can create corrugator bonding problems through dewatering of the adhesive before gelation, glueability problems through excessive absorption of the glue, and an increase in ink consumption (McGrattan 1990a; McGrattan 1990b).

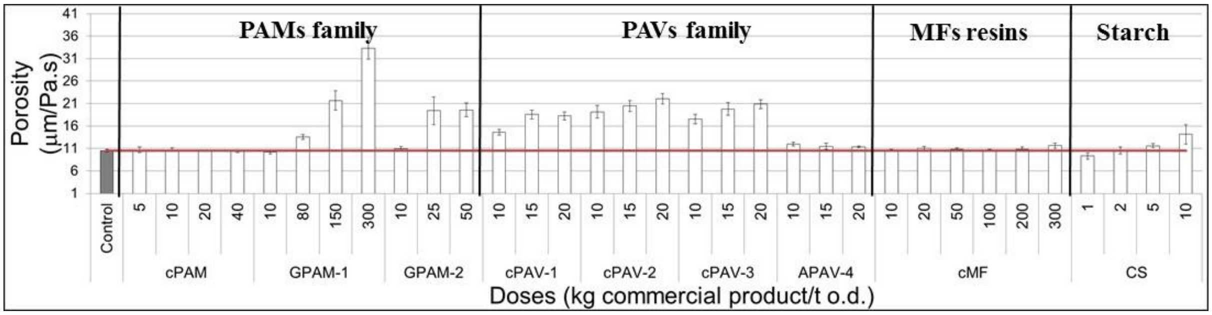

Fig. 3. Porosity with different doses of additives

Effect of CNF-E and CNF-P on Mechanical and Physical Properties

The CNF-E increased the bursting index of the OCC, achieving a maximum value at 4.5 wt.%, which was over 50% higher than without CNF. However, increasing amounts of CNF-E achieved lower increases in bursting strength index. At a dose of 4.5 wt.% of CNF-P, an increase of close to 46% was achieved in bursting strength index. This increase in bursting strength index was higher at a dose of 6 wt.% of CNF-P, reaching up to 52%.

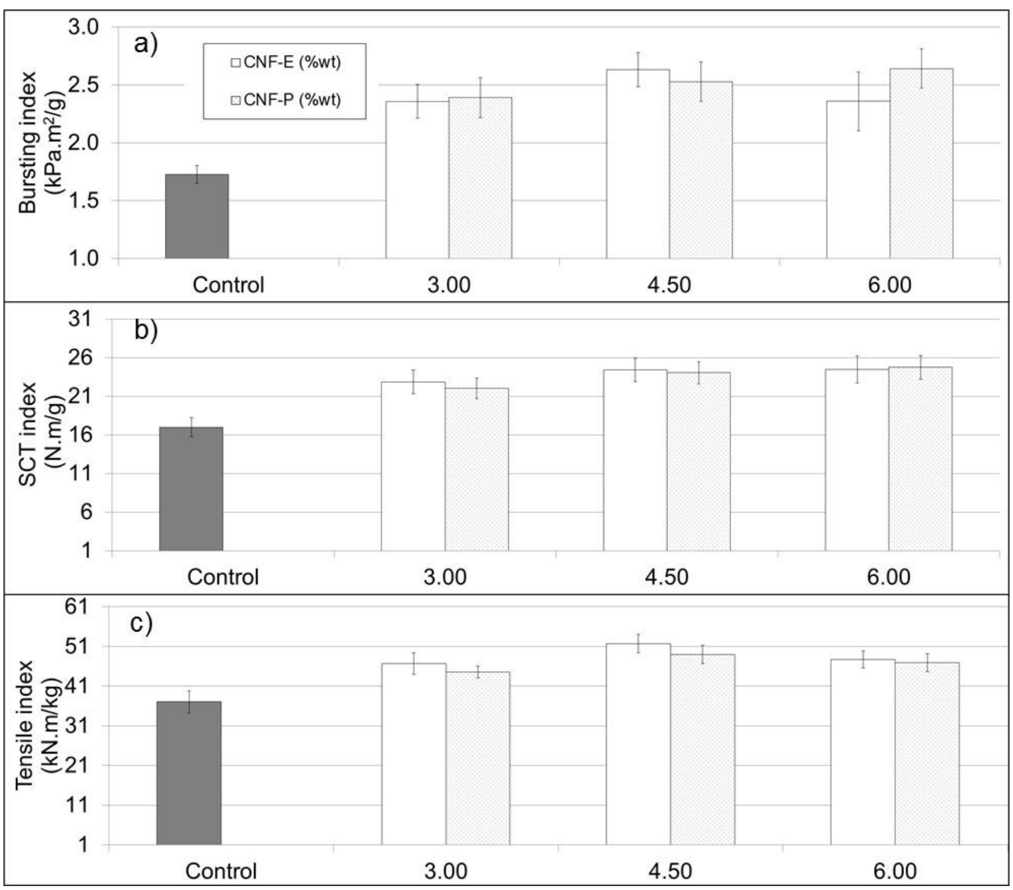

Fig. 4. Bursting (a), SCT (b), and tensile (c) indexes with different doses of CNF-E and CNF-P

Nevertheless, this dose is extremely high and would not compensate for the slightly larger increase achieved in bursting strength index. The SCT index could be increased up to 40% by adding 4.5 wt.% of CNF to the pulp, and higher amounts of CNF maintained this increase. The tensile index of the handsheets also improved with increasing amounts of CNF, reaching the highest tensile index values at 4.5 wt.% for both types of CNF (Fig. 4). Therefore, considering all of the mechanical properties, the optimal CNF dose was 4.5 wt.% for both types of CNF studied.

Porosity was reduced by increasing doses of both types of CNF (Fig. 5). This effect on porosity was expected because nanofibrils position on the spaces between fibers and block the pores. Similar effects of CNF have been reported by Delgado-Aguilar *et al.* (Delgado-Aguilar *et al.* 2014) on deinked pulp and by other authors on virgin pulp (González *et al.* 2013). Therefore, the increase of strength properties and the reduction in porosity caused by CNF might reduce the need for high refining, avoiding high energy consumption and reducing costs (Delgado-Aguilar *et al.* 2014).

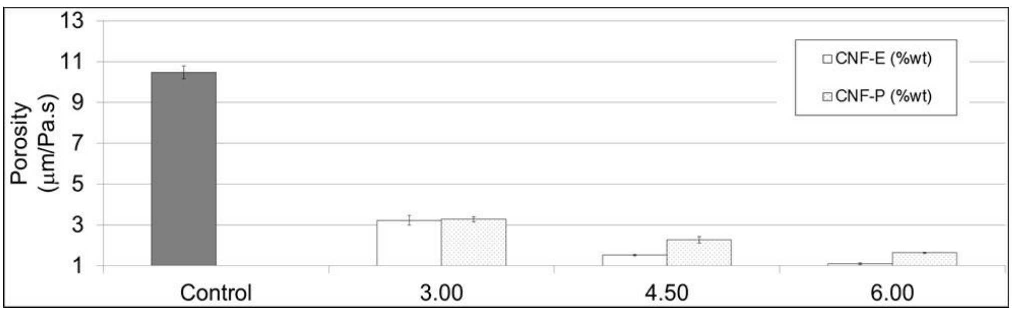

Fig. 5. Porosity with different doses of CNF-E and CNF-P

Table 4 summarizes the optimum dosages of each additive for strength improvement, including the enhancement in bursting strength, SCT index, and tensile strength indexes. PAMs family greater improved all mechanical properties of recycled OCC with double doses for cPAM and GPAM-1 than the optimum flocculation ones.

Table 4. Optimum Doses for Strength Enhancement and Strength Properties Increases

Strength additives	Optimum doses for strength enhancement (kg additive/t dry pulp)	ΔBursting index (%)	ΔSCT index (%)	ΔTensile index (%)
cPAM	40	58.25	30.49	32.58
GPAM-1	300	67.43	33.44	22.57
GPAM-2	25	34.56	16.01	7.39
cPAV-1	10	13.10	12.33	3.96
cPAV-2	20	6.57	4.66	0.97
cPAV-3	20	4.03	12.09	-
APAV-4	20	27.58	3.71	0.90
cMF	200	5.99	10.97	4.65
CS	10	28.76	12.63	6.88
CNF-E	45	52.47	43.77	39.51
CNF-P	45	46.33	41.57	32.24

A dosage of 25 kg of GPAM-2/t dry pulp was the optimum for both strength enhancement and flocculation behavior, decreasing nearly half both the bursting strength and the SCT compared to cPAM and GPAM-1. For the cPAV family, medium cationic charge PAV (cPAV-1) increased strength properties more than higher cationic charge PAVs aids (cPAV-2 and cPAV-3) with a dose lower than in flocculation trials and APAV increased up to 27% bursting strength at 20 kg of APAV/t dry pulp, but SCT and tensile index were not greatly increased. MF resin and CS did not noticeably improve the strength properties of recycled OCC pulp compare to the others additives in similar concentrations. The optimum strength enhancement dose for both CNF was 45 kg CNF/t dry pulp (4.5 wt.%). At 4.5 wt.% CNF, all strength properties of the recycled OCC were greatly improved.

Effect of the Combination of CNF and cPAM on Mechanical and Physical Properties

A new set of experiments with 45 kg CNF/t dry pulp (4.5 wt.% of CNF) and different doses of cPAM (20 and 40 kg/t dry pulp) was carried out to evaluate the effect of the CNF-cPAM combination on strength properties (Fig. 6)

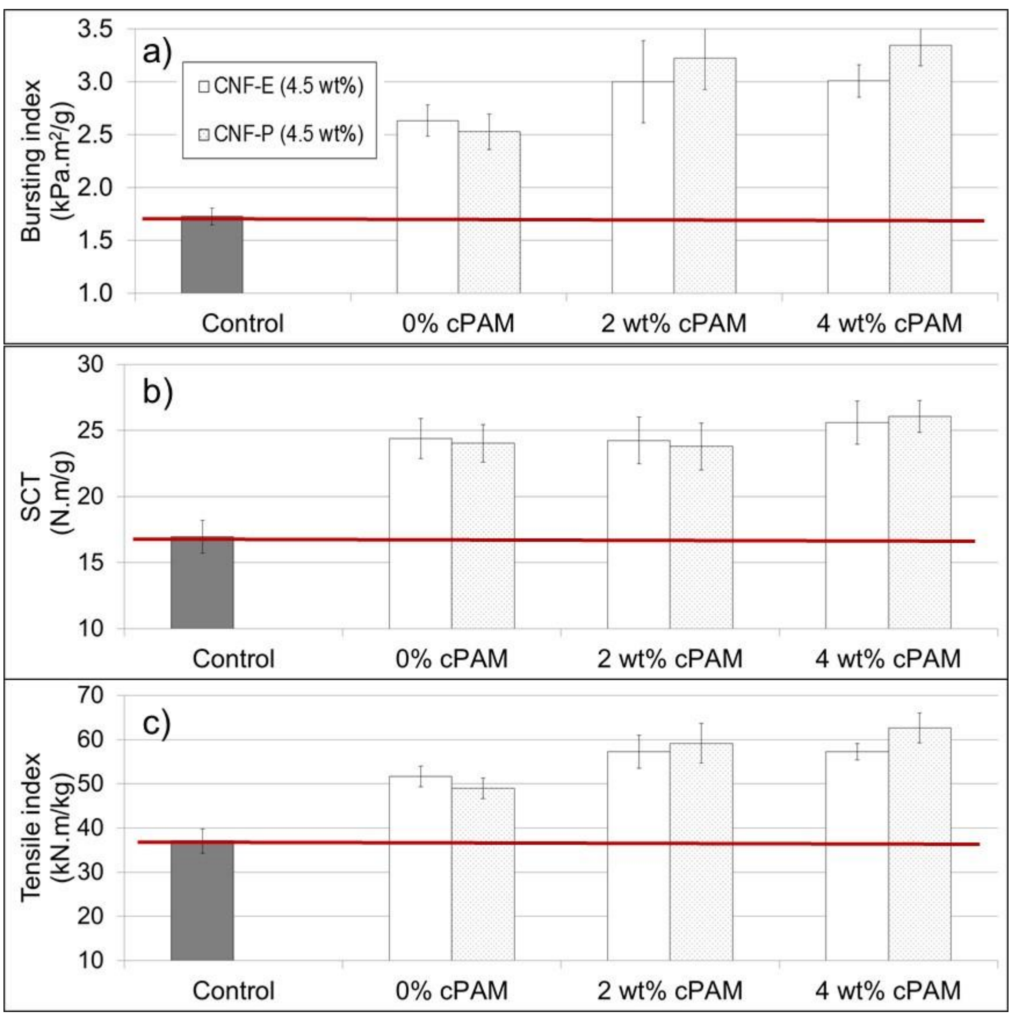

Fig. 6. Bursting (a), SCT (b), and tensile (c) indexes of the combination of different doses of cPAM and 4.5 wt.% of CNF using 0.5 wt.% cationic starch and 0.8 wt.% silica as retention agents

The combination of 4.5 wt.% of CNF-E (or CNF-P) and 2 wt.% of cPAM increased the bursting index of the handsheets approximately 74% and 87%, respectively. However, CNF-P caused the highest increase in this parameter, at almost 94%, when it was combined with 4 wt.% of cPAM. Lower differences were detected in the SCT index. The combination of 4.5 wt.% of CNF and 2 wt.% cPAM did not improve the SCT index compared with the handsheets with the same dose of CNF and without cPAM. Both caused around a 42% increase. The addition of 4 wt.% of cPAM to an OCC suspension with 4.5 wt.% of CNF achieved a slightly higher value of around a 50% increase in SCT, for both types of CNF studied. The tensile index showed differences between the CNF and their combinations with cPAM. The combination of CNF-P and cPAM achieved the highest increase in tensile index, at approximately 60% and 70% when 2 wt.% and 4 wt.% of cPAM were added, respectively.

In addition, the effect of the retention system (0.5 wt.% CS and 0.8 wt.% silica) on the mechanical properties was studied when the CNF and cPAM were combined at optimum strength doses. In presence of CNF, the retention system based on CS improved the mechanical properties of the recycled OCC and the strength increase were around 6% (Fig. 7).

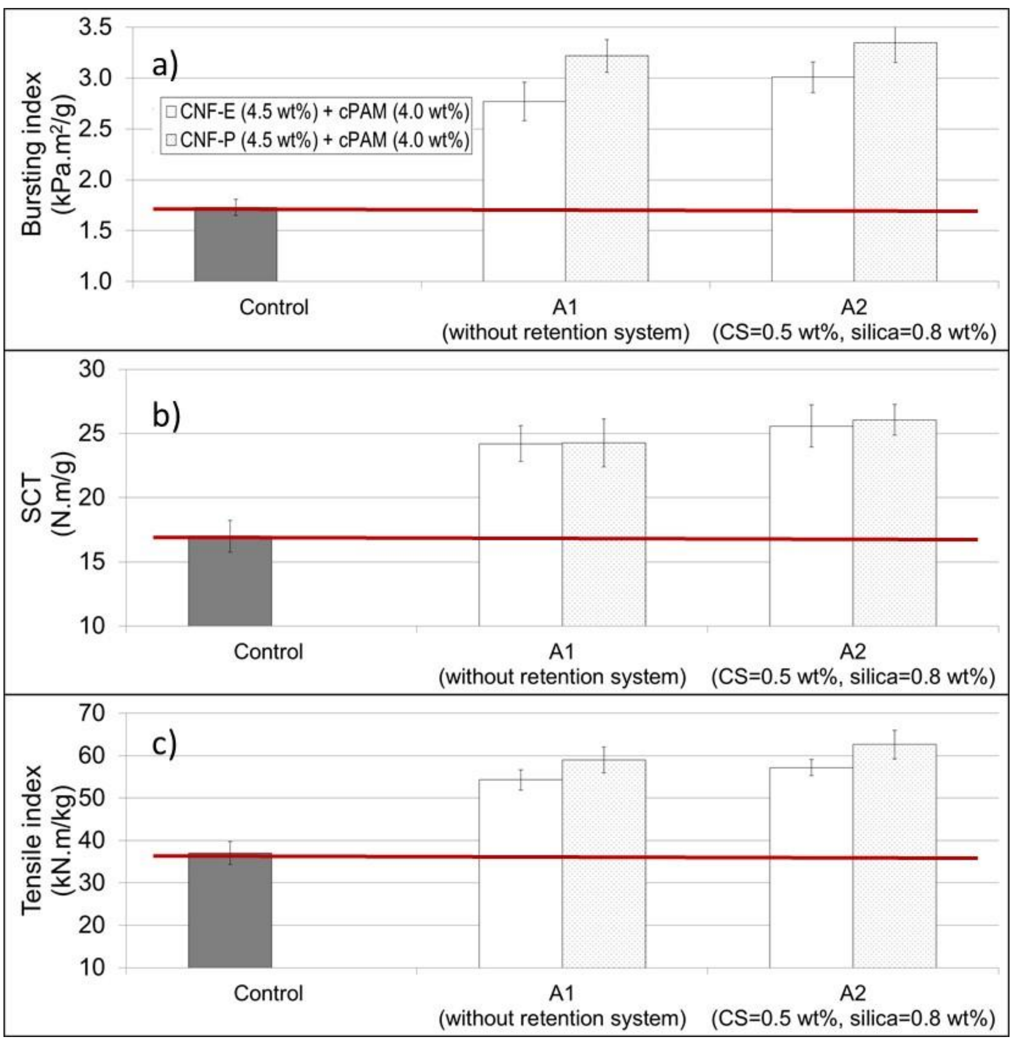

Fig. 7. Effect of the retention system (CS = 0.5 wt.%; silica = 0.8 wt.%) on mechanical strength properties using a combination of 4.5 wt.% CNF and 4.0 wt.% cPAM as strength aids

These results were aligned with the mechanical enhancement achieved when CS was added as strength additive to the recycled OCC pulp without CNF addition (Fig. 2), thus both specific bond strength and the bonded area were improved (Lindström *et al.* 2005).

The combination of CNF-P and cPAM reduced porosity more than the presence of CNF-E alone (Fig. 8). This effect on porosity indicated that CNF-P was better retained in the fiber network than CNF-E in the presence of cPAM and, therefore, slightly higher mechanical properties were achieved with the combination of CNF-P and cPAM. The entangled network of the CNF-P due to nanofibrils with higher length provided more joint points between CNF-P and cPAM fibers compared to CNF-E. Therefore, this reduction in porosity allows the use of high strength boards for unprinted liners, thereby avoiding runnability problems on corrugating machines or smearing during printing (McGrattan 1990a; McGrattan 1990b).

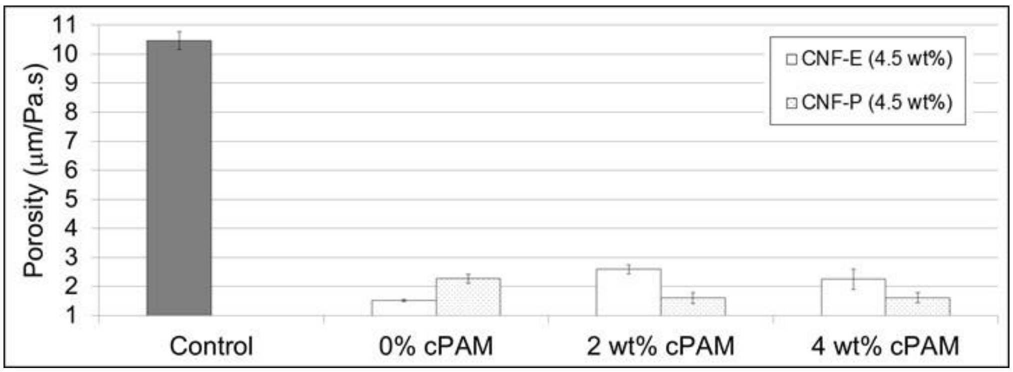

Fig. 8. Porosity of the combinations of different doses of cPAM and 4.5 wt.% of CNF in presence of the retention system (CS = 0.5 wt.%; silica = 0.8 wt.%)

CONCLUSIONS

1. Cellulose nanofibers, alone or combined with other strength aids, have great potential to enhance the mechanical properties of recycled OCC. Although the porosity of the final product was reduced, nanocellulose could be used for unprinted OCC liner applications. Additionally, the refining process of the fibers to improve the fiber interbonding could be reduced, decreasing the energy costs.
2. The PAM additives greatly improved all of the mechanical properties of recycled OCC. However, extremely high doses were needed for some cationic glyoxalated polyacrylamides, which would not be feasible for industrial use.
3. The optimal dose of cPAM and CNF for mechanical improvement was around 4 wt.%. However, the effects caused by both aids were not cumulative when they were combined.
4. The CNF-P were better retained in the fiber network than CNF-E in the presence of cPAM, and therefore, slightly higher mechanical properties were achieved when the combination of CNF-P and cPAM was used. The CNF-P reported the highest increase in bursting index when 4.5 wt.% was combined with 20 kg and 40 kg of cPAM/t dry pulp, achieving an increase of over 85% and 93%, respectively. The combination of

CNF-P and cPAM achieved the highest increase of tensile index, at almost 60% and 70% when 20 kg and 40 kg of cPAM/t dry pulp were added, respectively.

ACKNOWLEDGMENTS

The authors wish to thank the European project FP7-SME-2012-2-315633-Fibre+ and the Economy and Competitiveness Ministry of Spain for the support of projects CTQ2012-36868-C02-01 and CTQ2013-48090-C2-1-R.

REFERENCES CITED

Balea, A., Merayo, N., Fuente, E., Delgado-Aguilar, M., Mutje, P., Blanco, A., and Negro, C. (2016). "Valorization of corn stalk by the production of cellulose nanofibers to improve recycled paper properties," *BioResources* 11(2), 3416-3431. DOI: 10.15376/biores.11.2.3416-3431

Blanco, A., De la Fuente, E., Negro, C., Monte, M. C., and Tijero, J. (2002a). "Focused beam reflectant measurement as a tool to measure flocculation," *Tappi Journal* 1(10), 14-20. DOI: 10.1002/aic.14256

Blanco, A., Fuente, E., Negro, C., and Tijero, J. (2002b). "Flocculation monitoring: Focused beam reflectance measurement as a measurement tool," *Canadian Journal of Chemical Engineering* 80(4), 734-740. DOI: 10.1002/cjce.5450800403

Blanco, A., Miranda, R., and Monte, M.C. (2013). "Extending the limits of paper recycling: improvements along the paper value chain," *Forest Systems* 22(3), 471-483. DOI: 10.5424/fs/2013223-03677

CEPI. (2014). "Key Statistics. European Pulp and Paper Industry, " (http://www.cepi.org/topics/recycling), 1 June 2016

Chen, F. S., Huang, C., and Guo, Z. (2008). "Study on the systhesis of polyvinylamine (PVAm) and its application in papermaking," in: *2nd International Papermaking and Environment Conference*, Beijing, China, pp. 707-710.

Delgado-Aguilar, M., Gonzalez, I., Pelach, M.A., De La Fuente, E., Negro, C., and Mutje, P. (2014). "Improvement of deinked old newspaper/old magazine pulp suspensions by means of nanofibrillated cellulose addition," *Cellulose* 22(1), 789-802. DOI: 10.1007/s10570-014-0473-2

DiFlavio, J. L., Bertoia, R., Pelton, R., and Leduc, M. (2005). "The mechanism of polyvinylamine wet-strengthening," in: *13th Fundamental Research Symposium: Advances in Paper Science and Technology*, Cambridge, UK, pp. 1293-1316.

DIN 54358 (1981). "Testing of pulps; preparation of laboratory sheets for physical testing; Rapid-Köthen method," German Institute for Standardization, Berlin, Germany.

Eriksen, O., Syverud, K. and Gregersen, O. (2008). "The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper," *Nordic Pulp & Paper Research Journal* 23(3), 299-304. DOI: 10.3183/NPPRJ-2008-23-03-p299-304

Ghasemian, A., Ghaffari, M., and Ashori, A. (2012). "Strength-enhancing effect of cationic starch on mixed recycled and virgin pulps," *Carbohydrate Polymers* 87(2), 1269-1274. DOI: 10.1016/j.carbpol.2011.09.010

González, I., Boufi, S., Pèlach, M. A., Alcalà, M., Vilaseca, F., and Mutjé, P. (2012). "Nanofibrillated cellulose as paper additive in eucalyptus pulps," *BioResources* 7(4), 5167-5180. DOI: 10.15376/biores.7.4.5167-5180

González, I., Vilaseca, F., Alcalá, M., Pèlach, M.A., Boufi, S., and Mutjé, P. (2013). "Effect of the combination of biobeating and NFC on the physico-mechanical properties of paper " *Cellulose* 20, 1425-1435. DOI: 10.1007/s10570-013-9927-1

Hubbe, M. A., Venditti, R. A., and Rojas, O. J. (2007). "What happens to cellulosic fibers during papermaking and recycling? A review," *BioResources* 2(4), 739-788.

ISO 1924-3 (2014). " Paper and board - Determination of tensile properties - Part 3: Constant rate of elongation method (100 mm/min)," International Organization for Standardization, Geneva, Switzerland.

ISO 2759 (2014). " Board - Determination of bursting strength," International Organization for Standardization, Geneva, Switzerland.

ISO 5263-1 (2013). " Pulps - Laboratory wet disintegration - Part 1: Disintegration of chemical pulps," International Organization for Standardization, Geneva, Switzerland.

ISO 5269-2 (2004). "Pulps - Preparation of laboratory sheets for physical testing - Part 2: Rapid-Köthen method," International Organization for Standardization, Geneva, Switzerland.

ISO 5636-3 (2013). " Paper and board -- Determination of air permeance (medium range) -- Part 3: Bendtsen method," International Organization for Standardization, Geneva, Switzerland.

Johansson, C., Bras, J., Mondragon, I., Nechita, P., Plackett, D., Simon, P., Svetec, D. G., Virtanen, S., Baschetti, M. G., Breen, C., *et al.* (2012). "Renewable fibers and bio-based materials for packaging applications - A review of recent developments," *BioResources* 7(2), 1-47. DOI: 10.15376/biores.7.2.2506-2552

Laleg, M., and Pikulik, II. (1991). "Improving machine runnability and paper properties by a polymeric additive," *Journal of Pulp and Paper Science* 17(6), J206-J216.

Li, C. Y., Tang, Y. J., Wu, S., and Xue, G. X. (2010). "Change of chemical compositions of recycled OCC pulp and the fiber damage characterization," *Paper and Papermaking* 29(7), 25-28.

Lindström, T., Wågberg, L., and Larsson, T. (2005). "On the nature of joint strength in paper - A review of dry and wet strength resins used in paper manufacturing," in: *13th Fundamental Research Symposium*, Cambridge, UK.

Lu, S. J., Liu, R. X., and Sun, X. M. (2002). "A study on the synthesis and application of an inverse emulsion of amphoteric polyacrylamide as a retention aid in papermaking," *Journal of Applied Polymer Science* 84(2), 343-350. DOI: 10.1002/app.10340

Marais, A., and Wågberg, L. (2012). "The use of polymeric amines to enhance the mechanical properties of lignocellulosic fibrous networks," *Cellulose* 19(4), 1437-1447. DOI: 10.1007/s10570-012-9712-6

McGrattan, W. (1990a). "Key characteristics of linerboard, corrugating medium, and roll stock mechanical condition and their influence on the manufacture of corrugated products, Part 1," *Tappi Journal* 73(11), 99-108.

McGrattan, W. (1990b). "Key characteristics of linerboard, corrugating medium, and roll stock mechanical condition and their influence on the manufacture of corrugated products, Part 2," *Tappi Journal* 73(12), 76-80.

Miranda, R., Bobu, E., Grossmann, H., Stawicki, B., and Blanco, A. (2010). "Factors influencing a higher use of recovered paper in the european paper industry," *Cellulose Chemistry and Technology* 44(10), 419-430.

Miranda, R., Monte, M. C., and Blanco, A. (2013). "Analysis of the quality of the recovered paper from commingled collection systems," *Resources Conservation and Recycling* 72, 60-66. DOI: 10.1016/j.resconrec.2012.12.007

Nazhad, M. M. (2005). "Recycled fiber quality - A review," *Journal of Industrial and Engineering Chemistry* 11(3), 314-329.

Nazhad, M. M., and Sodtivarakul, S. (2004). "OCC pulp fractionation - A comparative study of fractionated and unfractionated stock," *Tappi Journal* 3(1), 15-15.

Osong, S. H., Norgren, S. and Engstrand, P. (2016). "Processing of wood-based microfibrillated cellulose, and applications relating to papermaking: A review," *Cellulose* 23(1), 93-123. DOI: 10.1007/s10570-015-0798-5

Pelton, R. (2004). "On the design of polymers for increased paper dry strength - A review," *Appita Journal* 57(3), 181-190.

Saito, T., Kimura, S., Nishiyama, Y., and Isogai, A. (2007). "Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose," *Biomacromolecules* 8(8), 2485-2491. DOI: 10.1007/s10570-010-9431-9

Son, D. J., and Yong, K. B. (2005). "Improvement of wet-end performance and paper strength with polyvinylamine," *Journal of Korea TAPPI* 37(5), 63-69.

Taipale, T., Österberg, M., Nykänen, A., Ruokolainen, J., and Laine, J. (2010). "Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength," *Cellulose* 17(5), 1005-1020. DOI: 10.1007/s10570-010-9431-9

TAPPI T 826 pm (1992). "Short span compressive strength of containerboard," TAPPI Press,Atlanta, GA.

Wang, G. Y., and Jing, Y. (2014). "Synthesis and application of a cationic polyacrylamide dry strength agent with anionic content," *BioResources* 9(1), 1111-1120. DOI: 10.15376/biores.9.1.1111-1120

Wang, S. L., Wang, M., and Chen, F. S. (2015). "Synthesis of poly vinylamine-co-(sodium acrylate) and its application as a paper strength additive," *BioResources* 10(1), 750-759. DOI: 10.15376/biores.10.1.750-759

Yamauchi, T., and Hatanaka, T. (2002). "Mechanism of paper strength development by the addition of dry strength resin," *Appita Journal* 55(3), 240-243.

Yuan, Z. Y., and Hu, H. R. (2012). "Preparation and characterization of crosslinked glyoxalated polyacrylamide paper-strengthening agent," *Journal of Applied Polymer Science* 126, E458-E468. DOI: 10.1002/app.36779

Yuan, Z. Y., Hu, H. R., and Wen, Y. B. (2011). "Synthesis and application of glyoxalted polyacrylamide paper strengthening agent," in: *Application of Chemical Engineering, Pts. 1-3*, Z. Cao, Y. H. He, L. Sun, and X. Q. Cao (eds.), Trans Tech Publications Ltd., Stafa-Zurich, pp. 1385-1390. DOI: 10.4028/www.scientific.net/amr.236-238.1385

Article submitted: June 1, 2016; Peer review completed: July 22, 2106; Revised version received: July 28, 2016; Accepted: July 29, 2016; Published: August 8, 2016.
DOI: 10.15376/biores.11.4.8123-8138